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Supplemental information: Nano-confinement of block copolymers in high accuracy topographical guiding patterns: Modelling the emergence of defectivity due to incommensurability

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Table of contents

1) Determining the crossover points from defect-free to defect-loaded state

One challenging part of this work is the accurate determination of the trench width w, at which the block copolymer system changes from one morphology to the other. We take advantage of the finite he length of the mask transmission gratings and therefore of the interference pattern.We observe that the feature widths become successively thinner towards the border of the pattern. In these last micrometres towards the border of the guiding pattern the features become thinner at a rate of roughly 1 nm per 100 nm. These structures are ideal to determine the trench widths, at which the self-assembly mode changes from one morphology to the other. Some example of border parts of the guiding patterns are depicted in figure S1 a)-c).

To minimize measurement uncertainties, we extract trench widths from 49 morphology changes.

The results of this analysis is summarized in the table below.

Group x → Group y	**Mean [nm]**	**Std Dev [nm]**	**Nat pitch [nm]**	**# Chain [-]**	**Chain Length [nm]**	**Delta Chain Length [nm]**	**Delta Chain Length [%]**
1→ 2	76.25	1.75	70.2	6	12.7	1.00	8.6
2→3	87.3	2.49	93.6	8	10.9	0.78	6.7
3→ 4	100.8	1.74	93.6	8	12.6	0.90	7.7
4→ 5	107	1.80	117	10	10.7	1.00	8.5
5→ 6	126.4	0.89	117	10	12.6	0.94	8.0

Table S 1: Analysis of CD/LWR/LER guiding patterns.

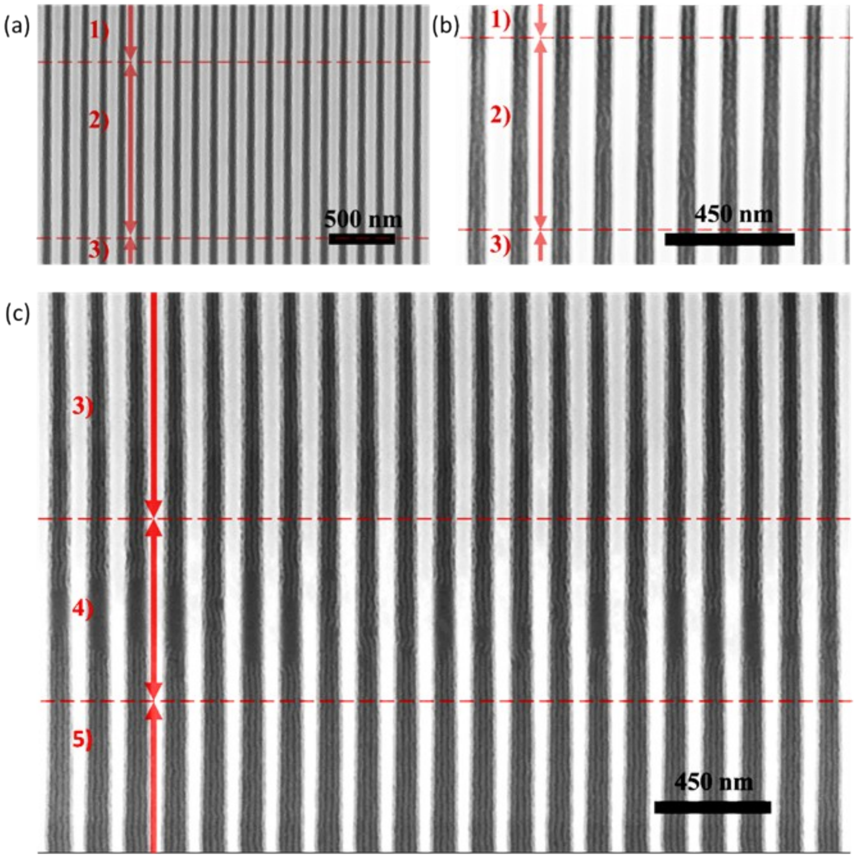

Figure S 1: Examples of how to determine the cut-off values for each group. The numbers in the images indicate which group this part of the guiding pattern belongs to. The dashed line indicates the approximate location of the cut-off value..

2) Determing the free energy for the defect-free and the defect loaded state

2.1) Adapting the free energy model for block copolymers confined between two plates according to Turner to our system

According to Turner, the free energy per block copolymer chain of a system confined between two parallel plates and normalized to the bulk free energy can be written as [1,2]:

$$\frac{e_{Turner}}{e_0} = \frac{1}{3}\left(\lambda^2 + \frac{2}{\lambda} + \frac{2 * \Gamma}{n * \lambda}\right) \quad (1)$$

The energy per chain in this system is a function of the parameters λ (which indicates the incommensurability of the trench with respect to an integer multiple of the natural pitch of the block copolymer; see formula (2)) and Γ (which balances the interface energy between one of the blocks and the confining wall, and the interface energy between the two blocks; see formula (3)).

$$\lambda = \frac{w}{n * L_0} \quad (2)$$

$$\Gamma = \frac{\gamma_{SiO_2 - PMMA}}{\gamma_{PS - PMMA}} \quad (3)$$

The interface free energy between two materials can be calculated by an extension of the Young's equation, as presented by Owens and Wendt. [3] The required parameters to do the calculus are the dispersive and polar contributions to the surface free energy of the respective materials.

$$\gamma_{A-B} = \left(\sqrt{\gamma_{P,A}} - \sqrt{\gamma_{P,B}}\right)^2 + \left(\sqrt{\gamma_{D,A}} - \sqrt{\gamma_{D,B}}\right)^2 \quad (4)$$

This calculus yields $\Gamma = 2.1$ using values extracted from refs. [4–6]. According to formula (1) and using the derived values, we can find the curves for the free energy per chain as a function of w , with n = {1; 2; 3; …}, where n corresponds to the number of block copolymers domains across the trench. The corresponding curves are depicted in figure S2) in pink (n=2), brown (n=3), green (n=4), blue (n=5) and cyan (n=6). According to the Turner model,he preferred self-assembly mode is always the one that exhibits the minimum free energy per chain. This state is symbolized by the black dashed line. The light blue shaded area in figure S2 represents the trench widths that we have worked with in the course of our experiments and the beige boxes represent those zones, where we observe the defect-loaded state, which cannot be explained with Turner's formula.

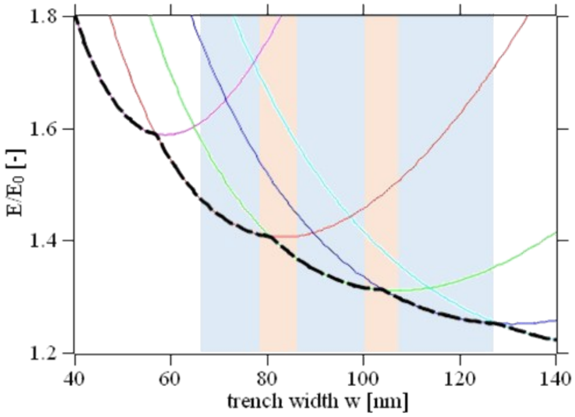

Figure S 2: Free energy per chain according to Turner. Colored parabolas: free energy per chain as a function of trench width w for n = {2;6} PS and PMMA domains. Black dashed curve: Minimum of all colored curves. Blue shaded area: Process window in this work. Yellowish shaded areas: Defect-loaded self-assembly.

2.2) Understanding the influence of Γ on the determination of characteristic points in the Turner model

Reliable information about the surface free energy of HSQ is somehow hard to find and we would like to probe the justifiable concern that inaccuracy has been introduced to the model due to that. Filling formula (2) into formula (1) yields

$$\frac{e_{vert}}{e_0} = \frac{1}{3}\left(\left(\frac{w}{n * L_0}\right)^2 + \frac{2 * n * L_0}{w} + \frac{2 * \Gamma * L_0}{w}\right) \qquad (5)$$

Accordingly

$$\frac{\partial\left(\frac{e_{vert}}{e_0}\right)}{\partial w} = 0 \qquad (6)$$

yields

$$w_0 = \sqrt[3]{\frac{n + 2 * \Gamma}{n^2 * L_0}} \qquad (7)$$

Therefore, we can tell that the location of the minimum free energy in a confined system for constant n is proportional to the cube root of Γ. Looking closely at figure S2, we observe surprisingly that the minimum free energy curve does not necessarily pass by the minima of the respective parabolas. The defect-loaded morphology of the block copolymers always occurs in the vicinity of crossover points between two of minimum free energy curves c_n and c_{n+1}. These points have the mathematical property

$$\left(\frac{e_{vert}}{e_0}\right)_n = \left(\frac{e_{vert}}{e_0}\right)_{n+1} \tag{8}$$

, which by plugging formula (5) into formula (8) becomes

$$\frac{1}{3}\left(\left(\frac{w}{n * L_0}\right)^2 + \frac{2 * n * L_0}{w} + \frac{2 * \Gamma * L_0}{w}\right) = \frac{1}{3}\left(\left(\frac{w}{(n+1) * L_0}\right)^2 + \frac{2 * (n+1) * L_0}{w} + \frac{2 * \Gamma * L_0}{w}\right) \tag{9}$$

.

Here the term containing Γ easily cancelles out. This means that an inaccurate estimation Γ does not affect the position of the local maxima of the minimum free energy curve.

2.3) Derivation of a model to predict the self-assembly mode as a function of the trench width

In this section we will explain, why block copolymers in certain trench width regimes abruptly change their morphology from stretched vertical lamellae with no or almost no defects to a state with a very high defect density. To do so, we will derive a mathematical expression that allows us to describe the free energy per chain normalized to e_0 in the defect-loaded state, fit it to our experimental data and compare it to the model presented by Turner. We assume that the block copolymer always self-assembles in the morphology with the minimum free energy.

Let us now assume that the free system we investigate is the sum of four energy components E_{tot}

$$E_{tot} = E_{S,L0} + E_{AB,\,L0} + E_{AW} + E_P \tag{10}$$

The components introduced above are defined as follows:

E_S: Energy stored in the stretching of the chains in bulk conditions

E_{AB}: Energy contribution due to the interface between the blocks A and B of the block copolymer in bulk conditions

E_{AW}: Energy contribution due to the interaction between the block A and the walls (we assume that only one block interacts with the wall [1,2])

E_P: An energy penalty that covers every possible energy component in our system that is not included in the first three terms, including mainly the formation of defects, but possibly also energetic components related to stretching and the increase of interface area. This term does not appear in any way in the model of Turner, because he does not consider any defects in his system.

As our system consists ofa number of b chains, we state that the total free energy of the system E_{tot} equals the product of b chains and their energy free energy e. This yields

$$E_{tot} = b * e \ = b * (e_{S,L0} + e_{AB,\, L0} + e_{AW} + e_P) \tag{11}$$

Minuscule letters refer to energies describing one chain, while capital letters refer to the energy of the entire system.

As Turner's model analyzes the energy per chain normalized to the bulk free energy, we will have to divide formula (11) by the number of chains and the energy of a single block copolymer chain in bulk configuration e_0, which yields

$$\frac{e}{e_0} = \frac{e_{S,\, L0} + e_{AB,\, L0} + e_{AW} + e_P}{e_0} = \frac{e_{S,\, L0} + e_{AB,\, L0}}{e_0} + \frac{e_{AW}}{e_0} + \frac{e_P}{e_0} \tag{12}$$

Because the sum of stretching energy and interface energy in bulk configuration is precisely defined as e_0, equation (12) can be simplified to:

$$\frac{e}{e_0} = 1 + \frac{e_{AW}}{e_0} + \frac{e_P}{e_0} \tag{13}$$

Now, let us have a closer look at the energy formula of Turner.

$$\frac{e_{Turner}}{e_0} = \frac{1}{3} * \left(\lambda^2 + \frac{2}{\lambda} + \frac{2 * \Gamma * L_0}{3 * w}\right) \tag{14}$$

The first summand in brackets accounts for the chain stretching, the second term accounts for the interface energy between the blocks and the third term corresponds to the energy contribution caused by the interaction between one of the block copolymer and the wall. Assuming that $\lambda = 1$ (the chains are perfectly commensurate, equation (2)) yields

$$\frac{e_{Turner}}{e_0} = \frac{1}{3} + \frac{2}{3} + \frac{2 * \Gamma}{3 * n} = 1 + \frac{2 * \Gamma * L_0}{3 * w} \tag{15}$$

In this way, we are capable of revealing the wall-block copolymer interaction term, and calculate the contribution of the wall-block copolymer interaction to the free energy per chain in the system (see eq. (16)).

$$\frac{2 * \Gamma * L_0}{3 * w} = \frac{e_{AW}}{e_0} = \frac{32.76\, nm}{w\, [nm]} \tag{16}$$

Thus, our term becomes:

$$\frac{e}{e_0} = 1 + \frac{32.76}{w} + \frac{e_P}{e_0} \qquad (17)$$

We furthermore assume that the value $\frac{e_P}{e_0} = const. \neq f(w)$. This term is likely to contain contributions originating from stretching energy and an additional energy component due to the formation of additional IMDS. It accounts for all the additional free energy components the block copolymers self-assembled in the defective state may be subject to. We know that the function we search for intersects with the curve derived by Turner exactly at the crossover points, where we observe the self-assembly morphology to change from the defect-free state to the defect-loaded state, and vice versa.

For this reason, we fit the curve

$$\frac{e}{e_0} = 1 + \frac{32.76}{w} + C \qquad (18)$$

to the five experimentally found crossover points depicted in figure S3. This analysis yields C=0.007074 with a coefficient of determination of R^2=0.9989. The curve represents the given data therefore excellently.

The curve that describes the self-assembly of block copolymers in a state with many defects is thus

$$\frac{e}{e_0}(w) = 1 + \frac{32.76}{w} + 0.007074 \qquad (19)$$

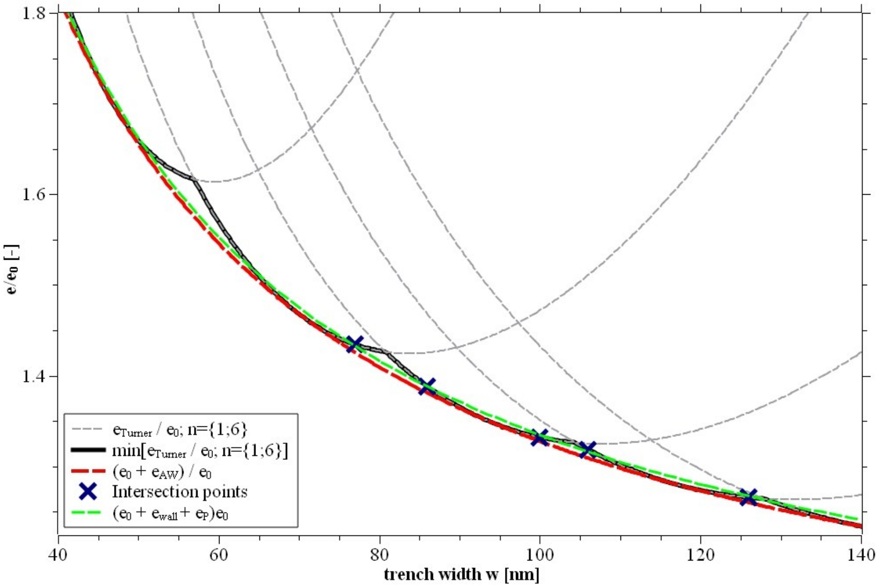

Figure S 3: Comparison of defect-free model as described by Turner, and the derived model for the defect-loaded state. Grey dashed lines: free energy for n={1;6}; black thick line: minimum of the grey parabola; red curve: sum of bulk free energy per chain and the free energy contribution by the polymer-wall interaction and green curve: fit of red curve plus an additional factor C to intersection points (blue crosses).

A comparison between Turner´s model (black) and our fit (green) is plotted in figure S3.

To fulfil the objective of this work and to find an expression that helps us predict, in which morphology the block copolymer self-assembles as a function of the trench width w, we will have a look at the energy difference between the two models denoted $\frac{\Delta e}{e_0}$, which is defined as follows.

$$\frac{\Delta e}{e_0} = \frac{e_{Turner}}{e_0} - \frac{e}{e_0} = min\left\{\frac{1}{3}\left(\left(\frac{w}{n * L_0}\right)^2 + \frac{2 * n * L_0}{w} + \frac{2 * \Gamma * L_0}{w}\right)\right\}_{n = \{i;j\}} - \left\{1 + \frac{32.76}{w} + 0.007074\right\} \tag{20}$$

This function is plotted in figure S 4 for the trench width w = {23.4 nm; 200 nm} and n = {1;9}. If the free energy of Turner´s model is larger than the free energy of the model that we have developed here, e.g. $\frac{\Delta e}{e_0}(w) > 0$, the curve plotted in figure S 4 is positive and the block copolymer self-assembles in the defective morphology. The light blue box in figure S4 represents trench widths that have been experimentally accessible for us. The yellow boxes indicate those trench widths, where the defect-loaded state is predicted to be energetically preferable. These areas become consistently narrower and are predicted to disappear entirely for trench widths larger than 130 nm. On a microscopic basis this is mainly due to the fact that upon stretching, the energy required to stretch a chain increases in a quadratic manner (see first summand in the Turner model). For this reason, in case of an incommensurable trench, the energy penalty is smaller if the system must stretch many chains a little bit, than if it has to stretch few chains a lot.

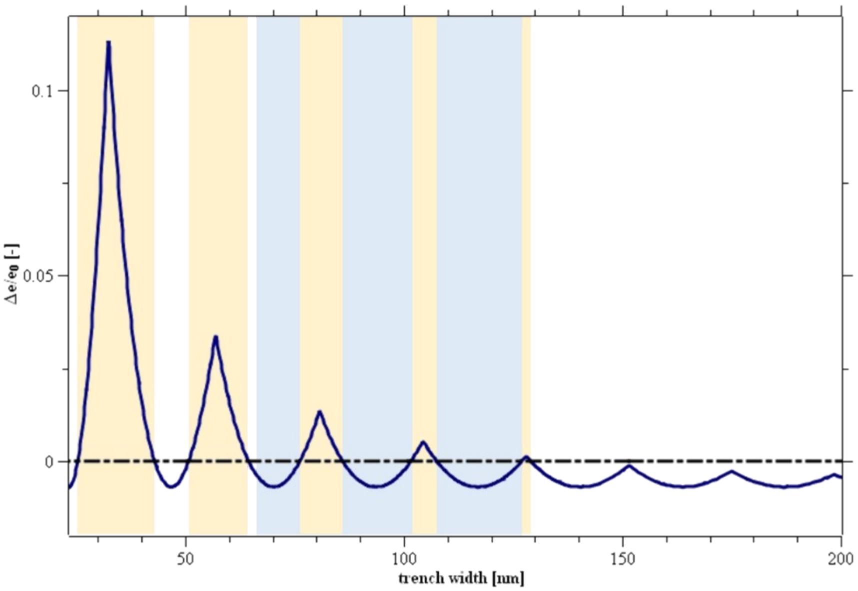

Figure S 4: Difference in free energy between Turner's model and the model derived in this document. A value $\Delta e/e_0<0$ indicates an energetic advantage of self-assembly in defect-free stretched lamellae, a value $\Delta e/e_0>0$ indicates an energetic advantage for the block copolymer to self-assemble in a defect-loaded state. The light blue box indicates the area for which we have experimental data available. The light yellow boxes indicate the area where we observe or predict the existence of the defect-loaded state.

2.4) Contributions to the free energy in block copolymers under nanoconfinement

Let us now understand which energy contributions play a role in the two models that we work with in this document. This will also help us to understand what the meaning of C is. This is a good opportunity to bear in mind, that in neither one of the models we included the interface energy contributions between the substrate and the block copolymer, and the surface tension of the block copolymer. As the two models we investigate are a form of upright-standing lamellae, both contributions are considered to be the same for both models.

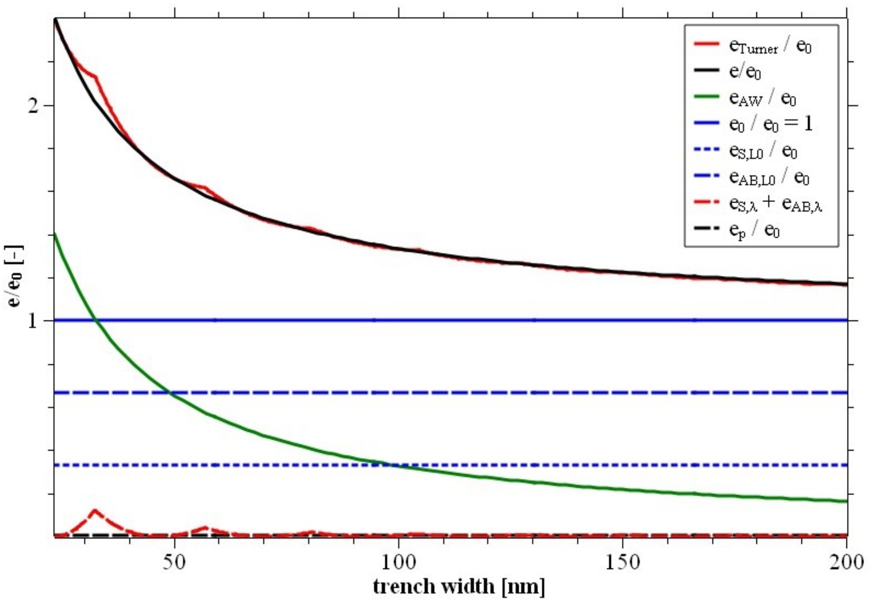

Figure S 5: Different energy components that contribute to the calculation of the free energy according to Turner and according to the model derived in this work.

Turner's model takes chain stretching (e_S), the inter-block interface (e_{AB}) and the block-wall interaction (e_{AW}) into account. The energy contributions of the chain stretching and inter-block interface can be understood as the sum of a bulk condition contribution ($e_{S,L0}$; $e_{AB,L0}$; $e_{S,L0}+e_{AB,L0}=e_0$) and a second contribution that accounts for the additional stretching (/compression) ($e_{S,\lambda}$) and the resulting reduction (/increase) ($e_{AB,L0}$) of interfaces due to the incommensurability λ.

$$\frac{e_{Turner}}{e_0} = \frac{e_S + e_{AB} + e_{AW}}{e_0} = \frac{(e_{S,\,L0} + e_{S,\lambda}) + (e_{AB,\,L0} + e_{AB,\lambda}) + e_{AW}}{e_0} = \frac{e_0 + e_{S,\lambda} + e_{AB,\lambda} + e_{AW}}{e_0} \tag{21}$$

The respective energy contributions are sketched in figure S 5. From this plot we learn that a great proportion of the free energy of the system originates from the bulk free energy $e_{S,L0}+e_{AB,L0}=e_0$ (blue curves). Another important, but strictly monotonically declining part of the free energy comes from the interaction of the A block (e.g. PMMA) and the wall (green curve). The characteristic 1/w-dependence of the curve can be explained by the constant free energy E_{AW} (equivalent to $2 * A * \gamma_{AW}$, where A is the area of the guiding pattern wall that is in contact with the preferentially wetting block of the polymer and γ_{AW} the corresponding interface energy) to be distributed to a consistently increasing number of chains for an increasing trench width. For an infinitely wide trench, this energy would become zero. The characteristic spikes in the Turner curve originate from the change in stretching and interface energy due to the incommensurability with the trench. It is natural that this curve is always positive, because the bulk free energy is by definition the minimum free energy as a function of the chain extension, and hence each deviation from this point leads to an energy penalty. Here, we only plot the sum of both contributions (represented by the red dashed line), which is always positive. The interface energy term, however, becomes negative in case of chain stretching, because the density of interface areas is reduced. In case of a chain compression, the interface energy term is positive, because the density of interfaces is reduced. This effect is the principle source of the different moduli for block copolymer compression and stretching.

Based on this analysis, let us now do the same analysis for the model we have developed to describe the defect-loaded system. Exactly like Turner´s model, our analysis takes the bulk energy as a starting point and analyzes the energetic deviation of the system from the bulk energy. Therefore, we also include both the bulk free energy ($e_{S,L0} + e_{AB,L0} = e_0$) and the wall interaction energy e_{AW}. Furthermore, our approach neglects the stretching of chains and the change in interface energy due to incommensurability and replaces it by a constant penalty term $\frac{e_P}{e_0}$. This term primarily accounts for the increase in free energy due to the creation of defects. Here the term "defect" refers both to the formation of wiggling and the formation of point-defect like artifacts in the crossover from n domains to n+1 domains.

$$\frac{e}{e_0} = \frac{e_{S,L0} + e_{AB,L0} + e_{AW} + e_P}{e_0} = \frac{e_0 + e_{AW} + e_P}{e_0} \qquad (22)$$

If we now subtract equation (22) from (21), we notice out that $\frac{\Delta e}{e_0}$ (plotted in figure S 4) can also be written as

$$\frac{\Delta e}{e_0} = \frac{(e_{S,\lambda} + e_{AB,\lambda}) - e_P}{e_0} \qquad (23)$$

This shows us that our results are independent of interaction energy of the block copolymer and the guiding pattern wall, and therefore independent of Γ. This finding is well recieved, given the fact that one of the major sources of uncertainty of our method consists in the estimation of Γ.

Previously, we have figured out that the $\frac{e_P}{e_0} = 0.00704$ which corresponds to a value of 0.704 % of e_0.

To set this value in a relation, let us now calculate the bulk free energy per chain as proposed by Ohta and Kawasaki [7,8] normalized to kT, which is given by:

$$\frac{e_0}{kT} = \frac{3}{8} * \frac{L_0^2}{N * a^2} + \frac{2 * N * a}{L_0} * \sqrt{\frac{\chi}{6}} = 2.99 \tag{24}$$

The block copolymer periodicity L_0=23.4 nm, N=424 and the Flory-Huggins interaction parameter χ=0.037.[9] For the determination of the average Kuhn segment length a of our block copolymer, we use 6.6 Å.[10]

Based on this calculus we estimate that

$$e_p = 0.00704 * e_0 = 0.021\ kT \tag{25}$$

We can thus conclude that the additional energy induced in the system compared to the bulk energy quantitatively only accounts for a relative small fraction of the total free energy of the system. Seen it the other way around, the energy difference per chain between the defective and the non-defective state in the directed self-assembly in topographical guiding patterns is defined by an energy penalty of a small fraction of kT. The value we estimate here is in surprisingly good agreement with the energy difference other authors have calculated for the defective and the non-defective state in the directed self-assembly of block copolymers in chemical guiding patterns.[11] This very small value demonstrates that the directed self-assembly of block copolymers relies on the system to accommodate to state that has a very small energy advantage with respect to other states, that are lithographically not useful.

3) References Supplemental Information

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